PETROGENESIS OF NATROCARBONATITE AT OLDOINYO LENGAI, EAST AFRICA—EVIDENCE FROM FE AND U ISOTOPE VARIATIONS

BY

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THESIS

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Abstract

Ol Doinyo Lengai (ODL), Tanzania, is the only active carbonatite volcano on earth. Cyclical activity that consists of quiescent natrocarbonatite lava flow, explosive silicate eruption and dormancy has been observed throughout the 20th century at ODL. From 2007 to 2008, ODL explosively erupted coexisting natrocarbonatites and nephelinites. Numerous studies have been aimed at understanding how ODL natrocarbonatite forms. Liquid immiscibility is a favored hypothesis although condensate fluid separation is an alternative model. However, the exact mechanism that forms the ODL natrocarbonatite remains unresolved.

We carried out Fe and U isotope analyses among a variety of ODL samples. Our sample set includes natrocarbonatite that erupted in 2005, 2 comingled tephras (mixture of natrocarbonatite and nephelinite) and a sequence of 8 nephelinite tephras that erupted in 2007-2008; as well as magnetites separated from 2005 natrocarbontite; Ti-andradites and clinopyroxenes that were separated from one of the nephelinite tephras. Our results show a lighter Fe isotope composition of natrocarbonatite (δ^{56}Fe of -0.08‰ relative to IRMM-14) compared to nephelinite tephras (-0.06 to 0.20 ‰ relative to IRMM-14). Magnetites yield heavier Fe isotope composition (0.03‰) than natrocarbonatite; Ti-andradite has the heaviest Fe isotope composition among all analyzed samples due to its enrichment in Fe^{3+}. U isotope results show that natrocarbonatite, has a δ^{238}U of -0.20 ‰ (relative to CRM-112A), being isotopically heavier than 8 nephelinite tephras (range from -0.32 to -0.41 ‰, relative to CRM-112A).

Fe isotope results may reflect the interaction between an upward-moving carbonate-rich melt with previous emplaced crystal mush zone, during which Fe^{2+} preferentially enters the carbonate-rich melt and leaves Fe^{3+} in the remaining crystal rich mush zone. The carbonate-rich

melt degases water as pressure drops causing the observed dry natrocarbonatite lava on the surface. U isotope results may be explained also as the role of melt interaction with the mush zone, with the soluble, ^{238}U rich U(VI) dissolved in the carbonate-rich melt ultimately causing the observed heavier U isotope composition in natrocarbonatite relative to the nephelinite.

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CHAPTER 1: INTRODUCTION

The global carbon cycle plays a fundamental role in earth's climate, with atmospheric CO_2 modulating temperature through the Greenhouse effect (Kasting, 1993; Kerrick, 2001). Volcanic contributions of CO_2 to the atmosphere are significant with CO_2 being the second most abundant volatile component of silicate melts (Kokh et al., 2017). CO_2 plays an integral role in controlling magmatic evolution processes in a range of geological settings on variety of timescales. As the direct product of CO_2-magma interaction, carbonatite magmas provide us with insight into CO_2 behavior in magmatic systems, thus contributing to our understanding of the global carbon cycle.

As the only active carbonatite volcano on earth, Ol Doinyo Lengai (ODL) in East Africa is a target of study. ODL more or less continuously effusively erupts sodium carbonatite lavas (natrocarbonatite), punctuated by explosive silicate magma eruptions (e.g. nephelinite) every 30-35 years. Although numerous works have been conducted trying to understand how ODL natrocarbonatite forms and how natrocarbonatite genetically links with associated nephelinite, the exact petrogenesis of ODL natrocarbonatite is still an outstanding question in igneous petrology.

New stable isotope techniques can potentially provide insight into carbonatite formation through the investigation of fractionation of stable metal isotopes. For decades, stable isotope fractionations under magmatic temperatures were assumed to be too small to be detected because the fractionation factor (α) was recognized to be inversely proportional to temperature squared ($\alpha \sim \frac{1}{T^2}$) (Urey, 1947). However, the development of new mass spectrometry techniques in the past ten years has led to the observations of measurable isotope ratio variation of both transition metal elements (e.g. Fe) as well as the heaviest natural element (U) within high temperature samples.

One of the most significant discoveries is that a heavy Fe isotope composition is observed in highly differentiated granitic rocks compared to the mean mafic earth (Poitrasson and Freydier, 2005). Poitrasson et al. (2005) suggested that granitic magmas may become isotopically heavier because reducing, Fe^{2+}-rich fluids with relatively light Fe isotope composition exsolve from the crystallizing melts, leaving relatively Fe^{3+}-rich materials with heavy Fe isotope ratios behind (Poitrasson et al., 2004; Poitrasson and Freydier, 2005). If that is the case, Fe isotope fractionation could potentially be an indicator of hydrous fluids role in differentiation in magmatic systems. Resolvable $^{238}U/^{235}U$ variations have also been reported in high temperature samples (Hiess et al., 2012; Weyer et al., 2008), although a convincing mechanism that drives the uranium isotope variations in high temperature conditions is still lacking. Notably, a recent study (Li et al., 2016) shows that heavier Mg isotope ratios occur in ODL natrocarbonatite relative to nephelinites. These authors use the Mg isotopic variations in a model advocating for a liquid immiscibility origin to the natrocarbonatite—the most often posed hypothesis for forming ODL natrocarbonatite. While the evidence for liquid immiscibility provided by the Mg isotope data is ambiguous based on discussion below, it is clear that significant variations in stable metal isotope ratios occur in this system, providing important new constraints on the petrogenesis of ODL magmas.

To investigate the mechanisms that form ODL natrocarbonatite and nephelinite, we performed high precision Fe (56/54) and U (238/235) isotope ratio analyses for various samples from ODL including a 2005 erupted natrocarbonatite, and a suite of nephelinites erupted in 2007 and 2008, as well as Fe-bearing minerals separated from these rocks. Our results demonstrate that significant variations of the Fe and U isotope ratios occur within the suite, presumably reflecting fractionations during the magma formation and differentiation processes of ODL

natrocarbonatite and nephelinite. These observations will be applied to explain the petrogenesis of natrocarbonatite.

CHAPTER 2: GEOLOGICAL BACKGROUND & SAMPLE SETTINGS

Ol Doinyo Lengai lies in the East African Rift Valley in Northern Tanzania (**Fig.1**). The volcano is composed largely of silicate lavas and pyroclastic rocks, with minor natrocarbonatite lavas and ashes. Ol Doinyo Lengai has a cyclical volcanic activity that consists of quiescent natrocarbonatite lava effusion, explosive silicate eruptions and dormancy (Dawson et al., 1995). Recent activity at ODL began with natrocarbonatite lava flows in 1983 continuing through 2007. Explosive eruption in 2007-2008 produced mostly nephelinite but have some carbonatite mixed in. During early 2008, a zoned nephelinite tephra having generally little natrocarbonatite component was erupted. Notably mixed in natrocarbonatite was found in the last erupted nephelinite from this eruption.

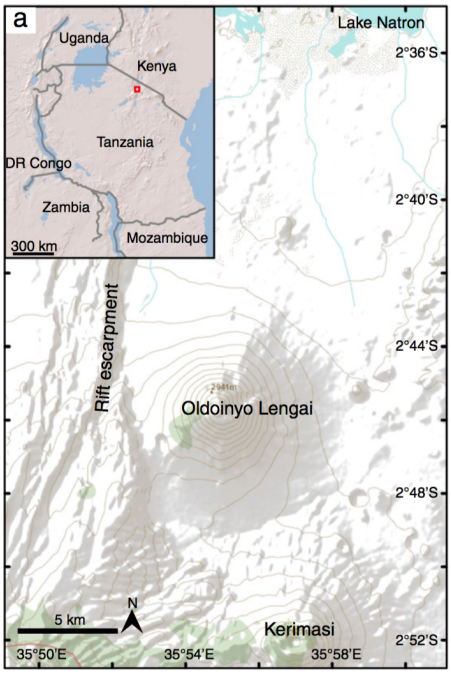

Fig.1 Geographical map showing the location of Ol Doinyo Lengai volcano (Bosshard-Stadlin et al., 2014)

The natrocarbonatite lava has extremely low eruption temperature (544-593°C) and low viscosity (1-5 Pa·s) that causes high velocities of flowing natrocarbonatite lava near the crater

(Dawson et al., 1995; Nielsen and Veksler, 2002). The natrocarbonatitic lava is characterized by abnormally high contents of alkali elements with (Na+K)/Al>1 (Dawson and Hill, 1998; Keller et al., 2006), especially for sodium (>30 wt.% Na_2O, Dawson et al., 1995; Keller and Krafft, 1990). Natrocarbonatite lava also contains high contents of barium, sulfur, chlorine, phosphorous and fluorine (Zaitsev et al., 2009). ODL natrocarbonatite contrasts with all ancient carbonatites observed on earth (mostly all intrusive rocks) that are rich in magnesium and calcium but depleted in alkalis.

ODL natrocarbonatite contains two alkali-rich and water-soluble carbonate minerals—gregoryite (ideally Na_2CO_3) and nyerereite [ideally $Na_2Ca(CO_3)_2$]. They form phenocrysts but also occur in the groundmass of natrocarbonatite. Other groundmass minerals are fluorite, sylvite and some accessory oxide such as magnetite.

ODL silicates (nephelinite) occur as carbonate-bearing tephras containing voluminous scoriaceous lapillis. The nephelinites are porphyritic in texture, mainly consisting of nepheline, wollastonite, combeite, Ti-andradite and clinopyroxene. The tephras are stratified, with the lower strata being more differentiated and subsequently erupted materials become progressively more primitive vertically. The compositional change of this zoning is counter intuitive to every other zoned magma body on earth because the more differentiated, first out nephelinite at ODL has lower silica content.

The close spatial and temporal relationships between natrocarbonatite and nephelinite imply petrogenetic linkage between natrocarbonatite and nephelinite. Given this unique volcanic system, numerous studies have been performed aimed at understanding how ODL natrocarbonatite forms and how natrocarbonatite interacts with nephelinite. A Sr-Nd-Pb isotope study (Dawson et al., 1995) and C-O-Li isotope study (Keller and Hoefs, 1995) both indicate that

natrocarbonatite ultimately is of mantle origin. However, melting experiments show that carbonate melt generated under mantle conditions is rich in magnesium and much less alkaline than ODL natrocarbonatite, which is rich in alkalis (>30 wt.% Na_2O and 10 wt.% K_2O, respectively) but depleted in magnesium (<0.5 wt.% MgO, respectively) (Sweeney et al., 1995). Thus, interpretations have focused on magmatic differentiation of mantle derived alkali basaltic magmas in the crust leading to carbonatite formation.

Natrocarbonatite could be generated by a liquid immiscibility reaction. Experiments performed by Freestone and Hamilton (1980) show that natrocarbonatite melt would be conjugate with a phonolite melt. Kjarsgaard et al. (1995) present experiments showing immiscible carbonatite melt coexists with silicate melt at a relatively low pressure (≦100MPa) and temperature (≦750°C) condition. However, temperatures of these experimentally generated immiscible carbonate melt remain significantly higher than observed eruption temperatures (~550°C). Alternatively, Nielsen and Veksler (2002) posit that the natrocarbonatite reflects generation as a fluid condensate produced when a volatile vapor phase forms during crystallization, separates and buoyantly rises and then condenses to form the erupted natrocarbonatite.

Studies of the H_2O-Na_2CO_3 binary system show that a single fluid (a hydrous melt) exists at 1 kbar and 500°C (Koster Van Groos, 1990). This is relevant given the observation that nepheline grains within ODL nephelinites have melt inclusions which have up to 10 wt. % H_2O (de Moor et al., 2013). In a study in progress at Illinois (Lundstrom et al. in prep), a set of thermal gradient experiments involving ODL nephelinite and Na_2CO_3-H_2O shows that an interconnected melt exists down to temperatures as low at 350°C; at 5 kb pressure, no vapor phase forms in these experiments. Thus, a plausible alternative model for various magmas

observed at ODL is that the natrocarbonatites form at the low temperature end of a continuously changing interstitial melt within a crystal mush under a thermal gradient within the ODL magma chamber. Because of buoyancy, these hydrous natrocarbonatites then percolate upward through the crystal mush eventually to be erupted as anhydrous natrocarbonatite due to H_2O degassing (de Moor et al., 2013).

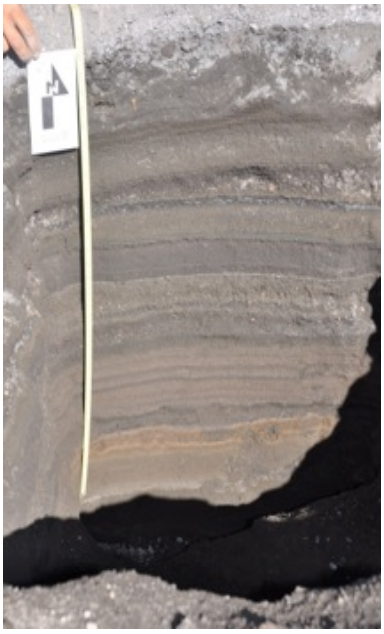

Fig.2 Silicate tephra profile of 2007-2008 eruptions. Photo was taken by T.P. Fischer

To understand the petrogenetic linkage between natrocarbonatite and nephelinite at ODL, we carried out high precision Fe and U isotope measurements for the 2005-2008 samples. Fe isotope analyses were performed for both ODL whole rocks and selected mineral separates. Whole rock samples include 1) natrocarbonatite erupted effusively in 2005; 2) selected strata from the stratified nephelinite tephras erupted in 2008 (ODL-8, from first erupted, most differentiated, lowest silica sample at the base of the profile; and ODL-1, the last erupted, least differentiated sample at the top of the profile which has carbonatite mixed in) (**Fig.2**); 3)

nephelinite tephras erupted in 2007 (ODL-#1, ODL-#2) that have significant comingled natrocarbonatite. Analyzed minerals include magnetites separated from natrocarbonatite OLD-2 and Ti-andradite and clinopyroxene separated from nephelinite sample ODL-4. U isotope analyses were performed for all ODL whole rock samples but not for separated minerals.

CHAPTER 3: ANALYTICAL METHODOLOGY

3.1 Mineral separations and analysis

Major element analyses were performed on different mineral separates (magnetite, Ti-andradite, clinopyroxene). Magnetite grains were separated from powdered natrocarbonatite using a parafilm covered Teflon-coated magnet. Natrocarbonatite powder attached to the magnetites was rinsed off the magnet with milli-Q water. Magnetites were then collected by separating the parafilm from the magnet. Ti-andradite and clinopyroxene were separated from crushed nephilinite by handpicking under an optical microscope. The compositions of separated minerals were measured using a Tescan Vega Scanning Electron Microscope equipped with an EDAX Octane Pro X-ray system (125 eV resolution at Mn) at Department of Geology at the University of Illinois at Urbana-Champaign (**Table-1**). Conditions include a 15 nAmp current and 15 KeV accelerating voltage. Standards based analysis with full ZAF corrections was used.

3.2 Sample dissolution and purification

All powdered samples and separated minerals were carefully weighed in Teflon beakers before being dissolved using acid digestion methods. Nephelinites (ODL-1 – ODL-8) and mineral separates were first digested with hydrofluoric acid while natrocarbonatite samples were first digested with 3N HNO_3. All samples were then treated by adding 3N HNO_3 and drying down followed by a similar 8N HCl treatment to remove fluoride precipitates. Given the high content of Ba and sulfate in the natrocarbonatite, precipitates of $BaSO_4$ were generated in solution. However, no Fe was detected in precipitates analyzed by the Scanning Electron Microscope (SEM). Therefore, we separated these precipitates from natrocarbonatite solutions by centrifuge.

For Fe purification, the solutions were dried down with concentrated HNO_3 and finally brought up in ~0.5ml 8N HCl. The HCl solutions were then passed through a HCl-conditioned anion exchange resin (AG-1-X8) for Fe purification. After loading samples onto the resin, matrix elements were removed by washing the resin with 9 column volumes of 8N HCl. Finally, Fe was eluted using 8N HNO_3 and 0.5N HCl. Purified samples were finally evaporated to dryness on a hot plate and then dissolved in 2% HNO_3 for Fe isotope analysis.

For U purification, the powered whole rock samples were dissolved in 3N HNO_3 and an amount of ^{233}U-^{236}U double spike solution with $^{233}U/^{236}U$ ~0.45 was added to the sample solutions. The purpose of the double spike is to correct the instrumental mass bias allowing a high precision U isotope analysis. The solutions were sealed in Teflon beakers overnight for equilibration and then evaporated to dryness. Samples were then brought up into 3N HNO_3 and passed through a 0.5ml column loaded with 3N HNO_3-conditioned UTEVA resin, followed by washing with 20 column volume of 3N HNO_3 to remove matrix elements. Th was separated by adding 5 column volume of 4N HCl. U was finally eluted and collected in 6ml of 0.1N HCl before being dried down on the hot plate. Samples were dried down again with 30ul of H_2O_2 and concentrated HNO_3 to remove organic compounds to improve analytical precision.

3.3 Mass spectrometer analysis

Fe isotope measurements were performed using a Nu-Plasma HR Multi-Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS) equipped with an ASX-110 Auto sampler and an Aridus-II Desolvating Nebulizer at Department of Geology at University of Illinois at Urbana-Champaign. After determining the Fe concentration of each sample using a ICP-mass spectrometry (on the Department of Geology's THERMO iCAPQ) and adjusting the

Fe concentration of both samples and standards to ~1 ppm ^{56}Fe, a 58-57 double spike was added.

The ^{56}Fe/^{54}Fe isotopic ratios are reported in delta notation relative to the standard IRMM defined by $\delta^{56}Fe = \frac{R_{sample}-R_{IRMM}}{R_{IRMM}} * 1000$ ‰, wherein R=^{56}Fe/^{54}Fe. Instrument mass bias was corrected using the ^{57}Fe-^{58}Fe double-spike (sample/spike ratio of ~2) with samples bracketed by and corrected to the IRMM-14 standard (Miller and Miller, 1988). Since Cr and Ni can be two interferences on the Fe isotopic analysis, chromium was measured on mass 52 to correct for interference of ^{54}Cr and Ni was measured on mass 60 to correct for ^{58}Ni in separate routines. A secondary standard UIFe ($\delta^{56}Fe$ =0.70±0.03‰, 2σ) as well as processed USGS (the United States Geological Survey) standard powders (BCR-2, AGV-1, COQ-1, RGM-1) were used as standards to check accuracy of offsets.

High precision U isotope analyses were also performed on the Nu-Plasma MC-ICP-MS equipped using a Nu Instrument DSN-100 Desolvating Nebulizer at Department of Geology at University of Illinois at Urbana-Champaign. The ^{238}U/^{235}U isotopic ratio was reported in delta notation relative to CRM-112A standard. To ensure the measurement accuracy, secondary standards CRM-129A and IRMM-18A were measured every three samples.

CHAPTER 4: RESULTS

4.1 Mineral compositional analyses

Magnetites separated from natrocarbonatite (OLD-2) were divided into two aliquots; one was used for major element analysis, the other was used for isotope analysis (see below). Major element analyses of three magnetite grains show that magnetite is nearly pure iron oxide with extremely low TiO_2 content (ranging from 0.13 wt.% to 1.95 wt.%) (**Table-1**). Major element compositions of Ti-andradite and clinopyroxene are also reported in Table.1.

4.2 Fe isotope ratios

Procedural blanks were less than 0.1% of the Fe content in the samples, a mass which is insignificant to resulting ratios. Measured δ^{56}Fe values for USGS standard materials are within 0.02‰ of published values indicating accuracy (**Table 2**). The overall precision of our measurements based on repeated samples is 0.01‰ (2σ).

Given this precision, analytically significant variations occur in samples. Fe isotope results were presented in Table-3 and were plotted against 1/FeO content in **Fig. 3**. δ^{56}Fe of natrocarbonatites (OLD-2) range from -0.07‰ to -0.09‰ with a mean value of -0.08; δ^{56}Fe of nephelinites (ODL-1 – ODL-8) range from -0.06‰ (ODL-1) to 0.20‰ (ODL-5 and ODL-8) (**Fig. 3**). An inverse trend between Fe isotope and FeO content can be observed (**Fig. 3**) ODL-1 has significant carbonatite content, consistent with its lower δ^{56}Fe.

Magnetites separated from natrocarbonatite (OLD-2) have heavier Fe isotope composition (0.03‰) than their hosting natrocarbonatite (-0.08‰) (Blue diamond in **Fig. 3**). The "residual" natrocarbonatite (OLD-2) after magnetite separation shows significantly lighter Fe isotope composition of -0.16‰, compared with -0.08‰ of "original" natrocarbonatite before

mineral separations. Clinopyroxene and Ti-andradite separated from nephelinite (ODL-4) have heavy Fe isotope compositions, with cpx of 0.10‰ and Ti-andradite of 0.42‰, respectively.

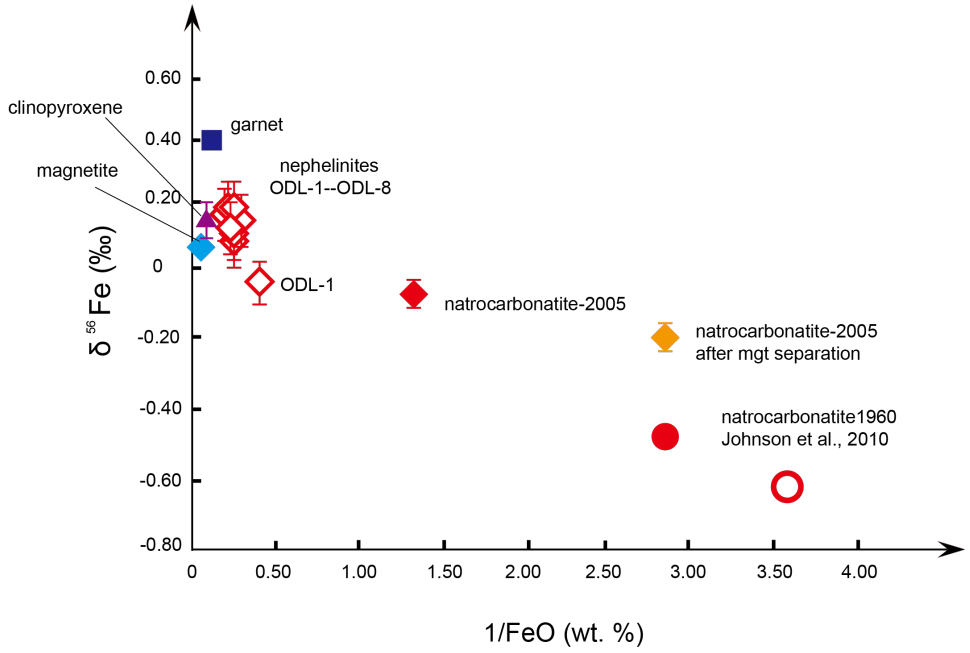

Fig.3 Plot of δ^{56}Fe with 1/FeO for variety of whole rock samples and separated minerals; Two Fe isotope data points (BD-114, BD-118) for carbonatite are from Johnson et al. (2010). Blue solid diamond represents magnetite data point; purple solid triangle is clinopyroxene data point; dark blue solid square is the Ti-andradite point; red empty diamonds are ODL nephelinite tephras, from ODL-1 to ODL-8; red solid diamond is the natrocarbonatite data point; yellow solid diamond is the natrocarbonatite after magnetite separation; red circles are natrocarbonatite that erupted in 1960, measured by Johnson et al. (2010)

4.3 U isotope ratios

The overall precision of U isotope measurements based on repeated standards is 0.06‰ (2σ). The accuracy of our analyses was assessed by offsets between different liquid standards measurements (CRM-112A, IRMM-18A and CRM-129). The averaged value for 4 IRMM-18A measurements is -0.18‰ and that for 2 CRM-129 measurements is -1.65‰, which are consistent with published data (Weyer et al., 2008). Similar to Fe isotope measurement, several USGS

materials (RGM-1, SGR-1) were analyzed prior to sample measurement. Measured $\delta^{238}U$ values for USGS standard materials are within 0.04‰ of published values indicating accuracy.

Given the precision, significant $\delta^{238}U$ variations occur in ODL samples. The variations were significant compared to previous terrestrial samples that have been reported in previous studies (Tissot and Dauphas, 2015; Weyer et al., 2008), as is shown in **Fig. 4**. U isotope results were presented in Table-4 and were plotted against 1/U content in **Fig. 5** (one filled diamond point represents natrocarbonatite extruded in 2005, empty diamond points represent nephelinite suite erupted in 2007-2008). Natrocarbonatite (OLD-2) has a heavier U isotope composition (-0.20‰) than 2007-2008 erupted nephelinites (ODL-1 – ODL-8, range from -0.30‰ to -0.41‰).

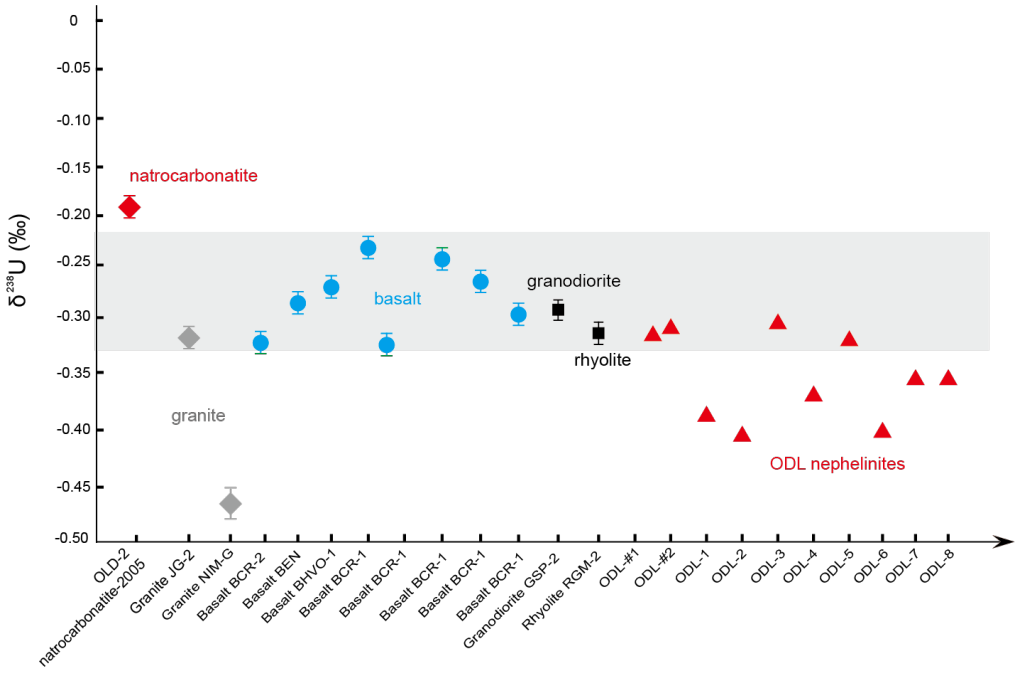

Fig. 4 Summary of delta values reported in previous research and from this study (red solid diamond is natrocarbonatite from this study; grey solid diamonds are two granite samples from Weyer et al., 2008; blue solid circle points are basalt sample from Weyer et al., 2008 and Tissot et al., 2015; black solid squares are granodiorite and rhyolite samples from Tissot et al., 2015; red solid triangle points are nephelinite tephra samples from this study)

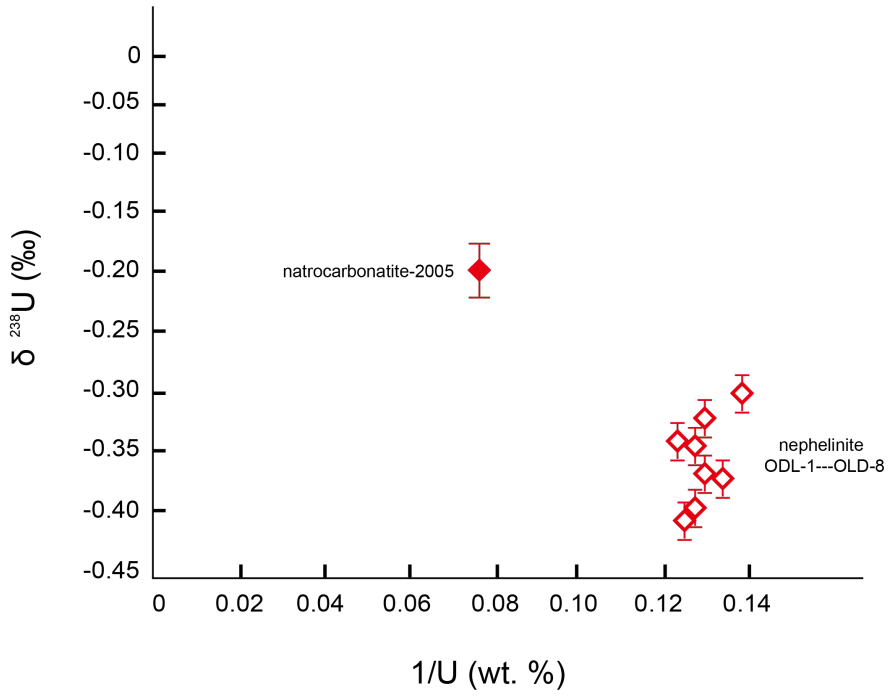

Fig.5 Plot of $\delta^{238}U$ with 1/U for natrocarbonatite (OLD-2) and 8 nephelinite tephras (ODL-1 to ODL-8)

CHAPTER 5: DISCUSSION

Here, the behavior of Fe and U isotope ratios among both whole rock samples and mineral separates during 2005-2008 time frame of the ODL system is used to gain insight into the petrogenetic processes at ODL. These two isotope systems are both sensitive to redox condition within the ODL nephelinite-carbonatite suite. A model is then provided for the petrogenesis of ODL natrocarbonatite and nephelinite based on Fe and U isotope variations.

5.1 Systematic Fe isotope variations among ODL rocks and minerals

Fe can occur in magmas in two different oxidation states (Fe^{2+} and Fe^{3+}), which should result in distinct isotope partitioning between different phases during magmatic evolution. These two species produce different bond strengths with the Fe^{3+} generally making stronger bonds which should incorporate heavier isotopes during equilibrium partitioning. Thus, Fe^{3+} rich phases such as magnetite and andradite should be isotopically heavier than coexisting melts.

For all ODL whole rock samples, δ^{56}Fe varies regularly with 1/FeO content (**Fig. 3**). This trend includes two older ODL natrocarbonatites that erupted in 1960 (BD-114, BD-118) analyzed by Johnson et al. (2010). Both these samples have considerably lighter Fe isotope ratios (-0.49‰, -0.62‰) than the natrocarbonatite that I measured (-0.08‰). However, both BD-114 and BD-118 also have considerably lower bulk FeO concentrations than OLD-2: BD-114 has 0.35 wt.% FeO and BD-118 has 0.31 wt.% FeO (Dawson et al., 1995), while OLD-2 has ~1 wt.% of FeO. These natrocarbonatite samples contain modal magnetite which should overwhelmingly dominate the FeO content of the bulk rock. For instance, the difference between 1 wt. % FeO and 0.35 wt. % FeO would correspond to a calculated difference of 1.23 % and 0.43 % in modal magnetite. Thus, the wide variation in natrocarbonatite whole rock FeO content (wt.%) and δ^{56}Fe

is most easily explained as slight variations in magnetite mode.

This conclusion is supported by the δ^{56}Fe and FeO behavior observed in the mineral separated natrocarbonatite sample (**Fig. 3**): the magnetite separated from OLD-2 has a heavier Fe isotope composition (0.03‰) than the bulk natrocarbonatite (-0.08‰) with a linear mixing relationship illustrated to the derivative natrocarbonatite (magnetite removed) which has the lightest Fe isotope ratio (-0.16‰). This is consistent with expectation that heavier Fe isotope ratios should occur in magnetite reflecting the Fe^{3+} rich nature of this phase. Based on the proportion and Fe content of mineral phases found in the natrocarbonatite, magnetite should dominate the iron budget.

Whether the modal magnetite variation in the natrocarbonatite whole rocks reflects differences in melt compositions (e.g. the magnetites crystallized from a carbonatite melt of whole rock composition) or reflects entrainment of magnetite crystals during ascent through a crystal mush cannot be to distinguish here. Regardless, these magnetites have very low TiO_2 contents (≦1 wt.%, respectively) (**Table 1**). The low TiO_2 content in magnetites suggest that the magnetite may equilibrate at temperature as low as ~500℃ based on an experiment performed by (Buddington and Lindsley, 1964) demonstrating the relationship between the formation temperature and mole percent of TiO_2 in magnetite as different fO_2. This is consistent with a late stage of the magma differentiation as proposed here.

The role of equilibrium isotope partitioning between mineral phases and melt in controlling Fe isotope systematics at ODL is further supported by mineral separates from the nephelinites. The Ti-andradites have a much heavier Fe isotope composition than whole rock nephelinites (ODL-4). This is also consistent with expectation of equilibrium isotope partitioning with a nephelinite-like melt because Ti-andradites are Fe^{3+} dominated minerals with measured

$Fe^{2+}/(Fe^{2+}+Fe^{3+})$ ratios ranging from 16.7% to 37.1% (Dawson and Hill, 1998).

5.2 U isotope variations in the ODL natrocarbonatite–nephelinite system

At ODL, $\delta^{238}U$ variations occur, with natrocarbonatite being isotopically heavier than nephelinites (**Fig. 5**), possibly reflecting the role of U redox state. Chernyshev et al. (2014) found that significant $^{238}U/^{235}U$ variations occur in minerals from hydrothermal uranium deposits. He suggested that possible uranium isotope fractionation happens during reduction of U(VI) to U(IV); the associated isotopic changes may reflect the nuclear volume effect (Bigeleisen, 1996; Schuessler et al., 2007; Stirling et al., 2007). Chernyshev et al. (2014) also indicated that the reduction process may cause the heavier ^{238}U to be concentrated in the U(IV)-bearing solid phase. Natrocarbonatite are characterized by low Nb/U ratio (**Fig. 6**), resulting in an observed correlation with $\delta^{238}U$ for the ODL system. One explanation for the low Nb/U is that Nb partitions strongly into some mineral relative to U as the carbonatite evolves via either fractional crystallization or other process such as element partitioning during fluid flow. If so, this element fractionation during partitioning may also control the U isotope behavior. Given the significantly distinctive Nb content in titanite (0.83 wt. %, Dawson and Hill, 1998) and in natrocarbonatite (<0.01 wt. %, this study), titanite could be the mineral that controls the low Nb/U ratio in natrocarbonatite. Titanite would incorporate Nb most strongly but would also incorporate U and could cause the observed isotope behavior and low Nb/U ratio.

Notably in an ongoing research at University of Illinois (Lundstrom et al., in prep), a set of thermal gradient experiments involving ODL nephelinite and Na_2CO_3-H_2O shows that an interconnected melt exists down to temperatures as low at 350°C; uranium was added in the system in order to trace the liquid transport process (because U is known to be enriched in the

ODL carbonatite). A uranium-bearing titanite grain was found in the low temperature end, which could give insight into the potential role of titanite partitioning on the uranium isotopic composition.

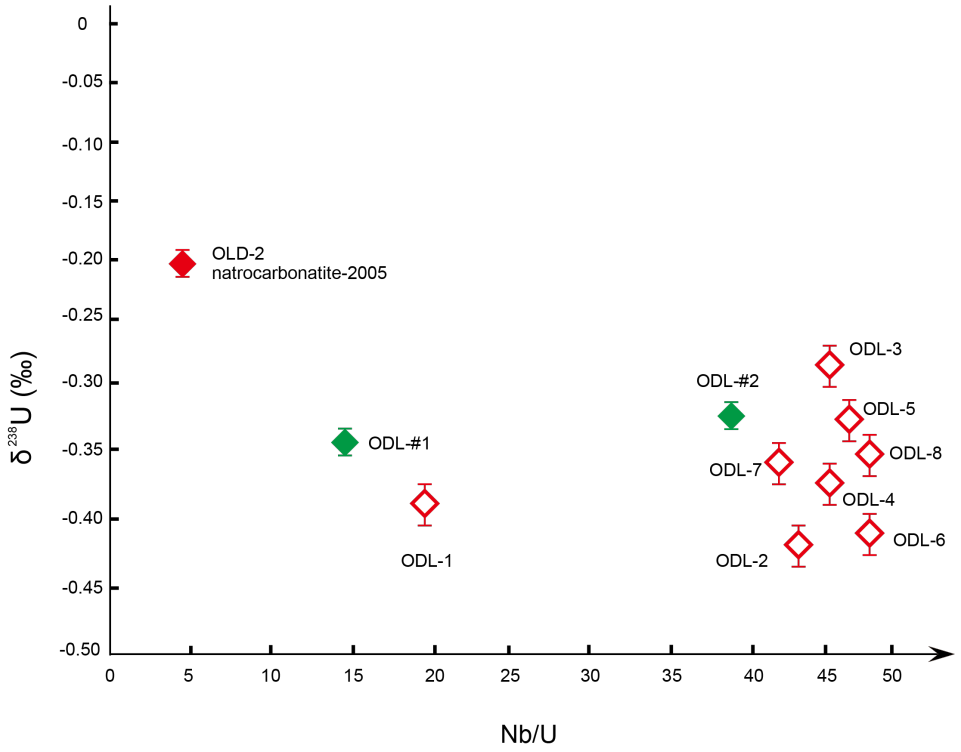

Fig.6 Plot of $\delta^{238}U$ with Nb/U for natrocarbonatite (OLD-2) and 8 nephelinite tephras (ODL-1 to ODL-8)

5.3 The implication of Fe isotope variations in the ODL system

Previous work has proposed that observed increases in $\delta^{56}Fe$ within igneous differentiation suites could potentially involve removal of a hydrous fluid during differentiation in a magmatic system (Heimann et al., 2008; Poitrasson and Freydier, 2005). During crystallization, a Fe rich fluid may saturate in the system and equilibrium isotopic partitioning occurs between coexisting crystals, hydrous fluid and melt. The presence of magnetite in the melt-crystal assemblage causes it to be isotopically heavy, which means the hydrous fluid becomes isotopically light (Poitrasson and Freydier, 2005). Removal of the "light" fluid results

in the melt plus crystal residue being heavy. In the case here, we view the fluid as being the natrocarbonatite.

While the ODL system was thought to be anhydrous based on the natrocarbonatite lavas being water-poor, de Moor et al. (2013) showed that ODL is a hydrous system based on the observation of > 10 wt.% water in melt inclusions in nepheline from nephelinites. In that work, they suggested that the natrocarbonatites may be derived from a hydrous carbonate liquid that degases H_2O at low-pressure conditions. Furthermore, experimental results of Koster Van Groos (1990) indicate the existence of H_2O-Na_2CO_3 (i.e. natrocarbonatite) melt at 1 kbar and 550°C conditions. Given the observation reported by de Moor et al. (2013) and the experimental result reported by Koster Van Groos (1990), hydrous fluid participation should be considered in the model of ODL natrocarbonatite petrogenesis. While Nielsen and Veskler (2002) proposed that ODL natrocarbonatite may originate from a fluid that condenses from a separated vapor phase, this model brings many questions such as how to explain the transport of many elements not likely to be vapor transported. Notably in the thermal gradient experiments described above (Lundstrom et al. in prep) a continuously changing melt composition appears to exist from temperatures of 1000°C to 350°C with the low temperature end presumably being a hydrous natrocarbonatite composition. Importantly, no vapor phase was observed in this 5 kbar experiment, meaning that there is no need to call upon formation of vapor followed by condensation. This solves the problem of how the carbonatite might become so enriched in trace elements and is consistent with the basic premise that the magma chamber mush is thermally zoned due to heat loss in the upper crust.

Here I propose a model that explains the observed Fe isotope variations in ODL samples that links the natrocarbonatite and nephelinites without the need to invoke an immiscibility

reaction. I suggest that nephelinite magmas pond and fractionate in the upper crust beneath ODL, forming a thermal gradient zone similar to the thermal gradient experiments (Lundstrom et al., in prep). Like the experiments, a continuously changing melt composition from nephelinitic at high temperature down to natrocarbonatitic at low temperature exists with the natrocarbonatite being similar to the sodium carbonate-H_2O melt observed by Koster Van Groos (1990). Thus, the melt forms an interconnected network within the crystal rich nephelinite magma body, resulting in the carbonatite buoyantly rising through the crystal mush. As it rises, the natrocarbonatite melt interacts with the crystal mush containing magnetite, Ti-andradite and clinopyroxene. Significant Fe isotope exchange happens during the fluid/melt's percolation through the crystal rich mush zone. Specifically, fluid percolation though crystal-rich mush would cause ferrous, isotopically lighter Fe to preferentially partition into the fluids, while heavy isotopes partition into magnetite and /or garnet; this process results in natrocarbonatite becoming isotopically light in Fe. The transfer of heavy Fe isotopes from natrocarbonatite to nephelinite crystals does not effectively alter the Fe isotopic composition of the nephelinite due to the Fe rich nature of the nephelinite bulk composition. Although measurements of magnetite-carbonatite fractionation factors do not exist at present, a possible analog would be the Fe isotope fractionation factor (Δ^{56}Fe of ~0.45) between magnetite-$FeCl_4^{2-}$ at 500°C reported by (Heimann et al., 2008; Polyakov et al., 2007; Polyakov and Mineev, 2000), wherein $FeCl_4^{2-}$ refers to the Fe species in the magmatic/hydrothermal fluid. It is suggested that the δ^{56}Fe value of exsolved Fe-chloride fluid will be ~0.1‰ heavier compared to the residual crystal mush (at 500°C). By assuming partitioning between magnetite and silicate minerals occurs at 500°C (Polyakov, Clayton, Horita, & Mineev, 2007), an estimate of the Fe isotope fractionation factor for ODL eruption temperature (~550°C) can be made. Assuming the average δ^{56}Fe value of the nephelinite, a δ^{56}Fe

of 1.6‰ would be predicted for magnetite, consistent with the interpretation that magnetite, associated with heavy Fe isotope, controls the Fe isotope partitioning process in ODL system.

Unfortunately, not much is known about U isotope fractionation in magmatic systems. U occurs at both U^{IV} and U^{VI} in magmatic system with minor U^{V}. If multiple valences existed, then isotopic fractionation might be expected between phases—fractionation occurs due to redox in low temperature settings—in groundwater, when U is reduced to $U^{IV}O_2$ (uraninite) it incorporates heavy U isotope (^{238}U) leaving the remaining U^{VI} with a light U isotope composition—this is thought to be due to the nuclear volume effect (Bigeleisen, 1996). However, it is unclear how much valence state variation there is in magmatic systems, how the different valence states go into different minerals and the mineral-melt fractionation factor associated with each. In general, in magmatic systems, U is an incompatible element with small mineral/melt partition coefficients for most mineral phases (<0.1, Farges et al., 1992). Notably, garnet is a mineral that can have relatively high mineral/melt partition coefficients (Beattie, 1994). Other mineral phases at ODL may also take in U (i.e. titanite, apatite). Titanite and apatite occur in ODL nephelinite tephras, meaning the crystal mush likely contains these minerals Following the template of Fe, we suggest that melt percolation through the crystal mush zone may cause U isotope redistribution between crystal pile and the melt. However, without knowledge of U isotope partitioning between the silicates and carbonate melt there is no ability to assess this suggestion.

The question of whether or not our model can explain Mg isotope observation that natrocarbonatite is heavier than nephelinite (Li et al. 2016) remains open. Theoretical calculations show that equilibrium Mg isotope fractionation will occur between different mineral phases, primarily reflecting coordination number and the strength of Mg-O bond (Huang et al.,

2013). Presumably, the carbonatite fluid percolating through the isotopically heavy garnet bearing crystal pile would cause Mg isotope partitioning, which would result in heavier Mg isotopes occurring in natrocarbonatite compared to the nephelinites, as is observed.

5.4 Assessment of liquid immiscibility

Liquid immiscibility in which an immiscible carbonate melt exsolves from a CO_2-saturated and strongly peralkaline nephelinitic melt remains a prominently proposed model for ODL (Freestone and Hamilton, 1980; Kjarsgaard et al., 1995; Lee and Wyllie, 1994; Mitchell, 2009). The observation of coexisting carbonate and silicate melt trapped as inclusions in nepheline phenocrysts from erupted ashes at Ol Doinyo Lengai (Mitchell, 2009) has been taken as evidence for liquid immiscibility by the advocates of the hypothesis. Clearly the natrocarbonatite and nephelinite coexist within the system so this observation may or may not be evidence for immiscibility. The isotopic observations here provide another piece of information to solve this debate.

Theoretically, the fractionation occurring between two immiscible melts at inferred temperatures of this process (700-1300°C) might be expected to be fairly small. At present there are no directly measured fractionation factors for immiscible carbonate-silicate melts. If bond strength controls isotopic fractionation, then a carbonate melt vs silicate melt fractionation would depend on the valence of the species partitioning or the coordination number of the elements in each fluid. In the most likely scenario of a magma chamber, the fO_2 is externally controlled such that strong differences in the proportions of distinct valence species should not occur between 2 coexisting liquids. Coordination number differences for Fe, U or Mg in carbonatite vs silicate melts are also unlikely to cause major fractionation. Finally, if previous melting experiments are

indicators of the temperature of the immiscible reaction, then fractionations will be much more muted during the immiscible melt reaction at 1000°C compared with the alternative proposed model (melt percolation and exchange with minerals at 500°C) simply because isotope fractionation factor is inversely related to temperature (Urey, 1947).

While experiments have been conducted to assess when and if carbonate melt and silicate melt show immiscible behavior as a function of temperature, pressure and composition (Freestone & Hamilton, 1980; Kjarsgaard et al., 1995; Brooker & Kjarsgaard, 2011), the results have not provided clear answers to the question of whether immiscibility forms natrocarbonatite at ODL. These experiments, in which synthetic natrocarbonatite and naturally formed nephelinite were sealed into capsules, were run at temperature ranging from 700°C (Kjarsgaard et al., 1995) to 1250°C (Freestone & Hamilton, 1980) and pressure ranging from 50 (Kjarsgaard et al., 1995) to 760 MPa (Freestone & Hamilton, 1980). Unambiguous identification of a carbonate melt is difficult because the carbonate melt never quenches to a glass but rather only forms dendritic aggregates of crystals upon cooling. The temperatures of experiments also point to the weakness that argues against the liquid immiscibility theory. The high experimental temperatures (700°C-1200°C) contrast with the low observed eruption temperature (~500°C) of ODL natrocarbonatite (Zaitsev et al., 2009). Furthermore, Nielsen et al. (2002) summarized compositions of conjugate carbonatite liquids at all investigated P and T conditions in these previous experiments showing that they have much lower $(Na_2O+K_2O)/(CaO+MgO+FeO)$ ratios and significantly higher SiO_2 content than those of natural natrocarbonatites.

In the model proposed, formation of two immiscible melts, a carbonate phase and silicate phase, is not required. The fluid-crystal mush interaction suggested by the alternative model could occur at shallow parts of the volcanic edifice that have relatively low temperature and

pressure condition. The Fe isotope composition of the ODL samples that we investigated are consistent with the Fe isotope partitioning expected in a magmatic system in when fluids are removed (Heimann et al., 2008; Poitrasson and Freydier, 2005). The U isotope composition of the ODL samples could provide additional evidence to support our model.

CHAPTER 6: CONCLUSIONS

1. This study firstly presents high precision Fe and U isotope data for recently erupted natrocarbonatites, peralkaline nephelinite as well as Fe-bearing mineral phenocrysts from Ol Doinyo Lengai, Tanzania. The natrocarbonatites that erupted in 2007-2008, have δ^{56}Fe values of (-0.08‰) that are lighter than coexisting nephelinite (from -0.06‰ to 0.20‰). Magnetites separated from natrocarbonatite show heavier Fe isotope signature than host natrocarbonatite. Ti-garnets have the heaviest Fe isotope composition among all the samples that we measured.

2. Both Fe and U isotope fractionation in ODL system may occur during carbonate melt percolation through previously emplaced crystal mush zone in the shallow part of the upper crustal magma chamber beneath ODL.

3. Observed Fe and U isotope variation in ODL system provides us insight into isotope fractionation at magmatic temperature.

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APPENDIX: TABLES

TABLE 1: Major element composition of separated minerals from ODL-4 (wt. %)

	Ti-andradite ODL-4:	*Clinopyroxene ODL-4:*	*Magnetite-1 OLD-2*	*Magnetite-2 OLD-2*	*Magnetite-3 OLD-2*
SiO2	29.11	44.16	-	-	-
FeO	19.53	25.17	99.58	99.87	98.05
CaO	40.29	22.42	-	-	-
MgO	-	3.83	-	-	-
Na2O	-	3.6	-	-	-
K2O	-	0.51	-	-	-
Al2O3	-	0.32	-	-	-
TiO2	11.07	-	0.42	0.13	1.95

Table 2: Comparison of δ^{56}Fe of standards measured at UIUC with literature data

Sources	USGS materials			
	BCR-2	AGV-1	COQ-1	RGM-1
Data measured in UIUC	0.08±0.02	0.10±0.04	-0.10±0.002	0.21±0.06
Huang et al. (2011)	0.09±0.01	0.15±0.03		
Craddock et al. (2010)	0.09±0.04	0.11±0.01	-0.12±0.03	0.22±0.01
Weyer et al. (2005)	0.08±0.05			
Poitrasson et al. (2004)	-0.01±0.08			
Heimann et al. (2008)		0.11±0.05		0.07±0.07

TABLE 3: Analyses of Fe isotope for ODL whole rock samples and separated minerals

Whole rock analyses:		**FeO content (wt.%)**	**δ^{56}Fe (‰)**
OLD-2-a	*2005 erupted natrocarbonatite*	1.26	-0.08±0.02
OLD-2-b	*2005 natrocarbonatite after magnetite separation*	0.33	-0.16±0.03
ODL-#1	*2007 tephra with mixed natrocarbonatite*	1.64	0.1±0.02
ODL-#2	*2007 tephra with mixed natrocarbonatite*	3.37	0.10
ODL-1	*2008 zoned nephelinite, at the top of the profile*	2.54	-0.06±0.01
ODL-2		5.78	0.1±0.004
ODL-3		5.86	0.16±0.01
ODL-4		5.55	0.13±0.05
ODL-5		5.58	0.20±0.01
ODL-6		5.21	0.15±0.06
ODL-7		5.51	0.1±0.08
ODL-8	2008 zoned nephelinite, bottom of the profile	5.58	0.2±0.08
Mineral Separates			
Magnetite from OLD-2		-	0.03±0.01
Ti-andradite from ODL-4		-	0.42±0.01
Clinopyroxene from ODL-4		-	0.1±0.06

TABLE 4. δ^{238}U of measured samples from Ol Doinyo Lengai

Sources	**USGS materials**		
	SGR-1	RGM-1	BHVO-1
Data measured in UIUC	-0.22±0.08	-0.32±0.08	-0.26±0.08
Weyer et al. 2008			-0.29±0.07
Tissot et al. 2015	-0.17±0.05	-0.31±0.09	-0.23±0.05
Whole rock	**Description**	**δ^{238}U (‰)**	
OLD-2	*2007 erupted natrocarbonatite*	-0.20±0.1	
ODL-#1	*mixed natrocarbonatites and tephras*	-0.33±0.1	
ODL-#2	*mixed natrocarbonatites and tephras*	-0.32±0.01	
ODL-1	*nephelinite, at the top of the profile*	-0.38±0.02	
ODL-2		-0.42±0.01	
ODL-3		-0.3±0.1	
ODL-4		-0.37±0.01	
ODL-5		-0.33±0.03	
ODL-6		-0.4±0.05	
ODL-7		-0.35±0.01	
ODL-8	*nephelinite, at the bottom of the profile*	-0.35±0.06	